IN THE SPECIFICATION:

Please replace paragraphs [0004], [0009], [0018], [0019], [0023], [0025], [0029], [0034], [0035], [0036], [0037], [0038], [0040], [0042], and [0043] with the following amended paragraphs.

[0004] Conventional chemical plating cells generally utilize an overflow weir-type plater containing a plating solution, which is also generally termed a catholyte herein. The substrate is positioned at the top of the weir during plating and an electrical plating bias is applied between the substrate and an anode positioned on a lower portion of the plating solution. This bias causes metal ions in the plating solution to go through a reduction that causes the ions to be plated on the substrate. However, one challenge associated with conventional plating cells is that the plating solution contains additives that are configured to control the plating process, and these additives are known to react with the anode during plating processes. This reaction with the anode causes the additives to ~~breakdown~~ break down, which generally renders the additives ineffective. Further, when the additives ~~breakdown~~ break down and are no longer able to facilitate process control, then the additives essentially become contaminants in the plating solution. As such, the concentration of the additives in the plating solution is constantly varying as a result of consumption in the plating process. This consumption of additives is generally addressed via a dosing mechanism configured to dose additives into the plating solution in response to consumption. However, one challenge associated with the dosing methodology is that it is difficult to maintain a constant concentration of additives, as the measurement and dosing processes take a substantial amount of time. Therefore, by the time the measurement is taken and the bath is dosed, the concentration has already changed. As such, the dosing system tends to chase the desired concentrations and is subject to substantial fluctuation.

[0009] Embodiments of the invention may further provide an electrochemical plating cell. The cell includes a fluid basin configured to contain an electrolyte plating solution, a fluid tank in fluid communication with the fluid basin and ~~being~~ configured to

supply the electrolyte plating solution thereto, and an electrolyte solution stabilization device in fluid communication with the fluid tank. The stabilization device includes a fluid container having a fluid inlet and a fluid outlet, and an absorbent material positioned in the fluid container in a fluid path between the fluid inlet and the fluid outlet, wherein the absorbent material is configured to leach a solution additive into the electrolyte plating solution to maintain the solution additive within a processing window during an electrochemical plating process.

[0018] Embodiments of the invention generally provide ~~and~~ an electrochemical plating system, wherein the electrochemical plating cells of the system includes an apparatus and/or method for dosing additives into the electrochemical plating solution with minimal concentration variation. Embodiments of the invention also provide an apparatus and method for preventing the additive breakdown concentration from increasing over time. The combination of maintaining a relatively constant additive concentration in conjunction with minimizing the breakdown concentration increase provides a plating cell that is capable of substantially eliminating plating defects resulting from additive dosing and breakdown.

[0019] Figure 1 illustrates a top plan view of an ECP system 100 of the invention. ECP system 100 includes a factory interface (FI) 130, which is also generally termed a substrate loading station. Factory interface 130 includes a plurality of substrate loading stations configured to interface with substrate containing cassettes 134. A robot 132 is positioned in factory interface 130 and is configured to access substrates contained in the cassettes 134. Further, robot 132 also extends into a link tunnel 115 that connects factory interface 130 to processing mainframe or platform 113. The position of robot 132 allows the robot to access substrate cassettes 134 to retrieve substrates therefrom and then deliver the substrates to one of the processing ~~cells~~ locations 114, 116 positioned on the mainframe 113, or alternatively, to the annealing station 135. Similarly, robot 132 may be used to retrieve substrates from the processing ~~cells~~ locations 114, 116 or the annealing chamber 135 after a substrate processing sequence is complete. In this situation robot 132 may deliver the substrate back to one of the cassettes 134 for removal from system 100. Additional

configurations and implementations of an electrochemical processing system are illustrated in commonly assigned United States Patent Application Serial No. 10/435,121 filed on December 19, 2002 entitled "Multi-Chemistry Electrochemical Processing System", which is incorporated herein by reference in its entirety.

[0023] Figure 2 illustrates a partial perspective and sectional view of an exemplary plating cell 200 that may be implemented in processing locations 102, 104, 110, and 112. The electrochemical plating cell 200 generally includes an outer basin 201 and an inner basin 202 positioned within outer basin 201. Inner basin 202 (also referred to as a weir) is generally configured to contain a plating solution that is used to plate a metal, *e.g.*, copper, onto a substrate during an electrochemical plating process. During the plating process, the plating solution is generally continuously supplied to inner basin 202 (at about 1 gallon per minute for a 10 liter plating cell, for example), and therefore, the plating solution continually overflows the uppermost point or weir of inner basin 202 and is collected by outer basin 201 and drained therefrom for chemical management and recirculation. Plating cell 200 is generally positioned at a tilt angle, *i.e.*, the frame ~~portion~~ member 203 of plating cell 200 is generally elevated on one side such that the components of plating cell 200 are tilted between about 3° and about 30°, or generally between about 4° and about 10° for optimal results. The frame member 203 of plating cell 200 supports an annular base member on an upper portion thereof. Since frame member 203 is elevated on one side, the upper surface of base member 204 is generally tilted from the horizontal at an angle that corresponds to the angle of frame member 203 relative to a horizontal position. Base member 204 includes an annular or disk shaped recess formed into a central portion thereof, the annular recess being configured to receive a disk shaped anode member 205. Base member 204 further includes a plurality of fluid inlets/drains 209 extending from a lower surface thereof. Each of the fluid inlets/drains 209 are generally configured to individually supply or drain a fluid to or from either the anode compartment or the cathode compartment of plating cell 200. Anode member 205 generally includes a plurality of slots 207 formed therethrough, wherein the slots 207 are generally positioned in parallel orientation with each other across the surface of

the anode 205. The parallel orientation allows for dense fluids generated at the anode surface to flow downwardly across the anode surface and into one of the slots 207.

[0025] Membrane 208 generally operates to fluidly isolate the anode chamber from the cathode chamber of the plating cell. Membrane 208 is generally an ionic or ion exchange membrane. The ion exchange membrane generally includes fixed negatively charged groups, such as $-SO_3$, -COO, HPO_{2-}, SeO_{3-}, PO_{32-}, or other negatively charged groups amenable to plating processes. Membrane 208 allows a particular type of ions to travel through the membrane, while preventing another type of ion from traveling or passing through the membrane. More particularly, membrane 208 may be a cationic membrane that is configured to allow positively charged copper ions (Cu^{2+}) to pass therethrough, *i.e.,* to allow copper ions to travel from the anode in the anolyte solution through the membrane 208 into the catholyte solution, where the copper ions may then be plated onto the substrate. Further, the cationic membrane may be configured to prevent passage of negatively charged ions and electrically neutral species in the solution, such as the ions that make up the plating solution and catholyte additives. It is desirable to prevent these catholyte additives from traveling through the membrane 208 and contacting the anode, as the additives are known to break down upon contacting the anode. More particularly, membranes with negatively charged ion groups like SO3- etc. not only to facilitate Cu ions transport from the anolyte to the ~~catolyte~~ catholyte, but also to prevent penetration of accelerators to anode. The accelerator is generally negatively charged organic ion: $^-$SO3- C3H6-S-S-C3H6-SO3$^-$, so it can't penetrate into or through the cation membrane. Further details of the membrane configuration of the plating cell may be found in commonly assigned United States Patent Application Serial Number 10/616,284, entitled "ELECTROCHEMICAL PROCESSING CELL", ~~under attorney docket number APPM/7669.P3, naming Michael X. Yang, Dmitry Lubomirsky, Yesdi N. Dordi, Saravjeet Singh, Sheshraj L. Tulshibagwale, and Nicolay Kovarsky as inventors~~ filed July 8, 2003, which is hereby incorporated by reference in its entirety.

[0029] As noted above, stabilization of additive concentrations in the electrochemical plating bath is a key component to maintaining acceptable plating

defect ratios. As such, embodiments of the invention utilize a novel plumbing and additive adsorption and desorption process to maintain the additive concentrations at their desired levels. More particularly, Figure 4 illustrates an exemplary plumbing configuration for an electrochemical plating cell of the invention. The plumbing configuration illustrates a plating cell 400 in the fluid communication with an electrolyte supply tank 404. The plating ~~sell~~ cell 400 includes a substrate support member configured to support a substrate 401 for processing, a porous diffusion member 403 positioned across the plating cell 400, and an anode 402 positioned in a lower portion of the plating cell 400. A plating solution or a catholyte solution is supplied to the plating cell by a fluid supply conduit 411 and returned to the electrolyte supply tank 404 via a return conduit 412. The return conduit 412 includes an absorbent container 403 and a filter 406. Filter 406, which may generally be a fluid permeable filter configured to trap particulates, operates to prevent the electrolyte entering the electrochemical cell from containing small absorbent particles that can penetrate into the electrolyte stream. Fluid pressure may be provided to both the supply and return conduits via a pump 407.

[0034] The anolyte solution (the solution supplied to the anolyte loop illustrated in Figure 5 and Figure 2) is generally contained in the volume below the membrane 208 and above the anode. The anolyte solution may be simply the catholyte solution without the plating additives, *i.e.*, levelers, suppressors, and/or accelerators. However, the inventors have found that specific anolyte solutions, other than just stripped catholyte solutions, provide a substantial improvement in plating parameters. Specifically, use of the specific anolyte solutions improves the copper transfer through the membrane and prevention of copper sulfate and hydroxide precipitation, *i.e.*, when the Cu ions transport through the membrane, copper sulfate accumulates in the anolyte and starts to precipitate on the anode provoking its passiviation ~~are improved~~. When pH of the anolyte is maintained above about 4.5 to about 4.8, copper hydroxide starts to deposit from Cu salt solutions, *i.e.*, Cu2+ + 2H2O = Cu(OH)2 (deposit) + 2H+. More particularly, the inventors have found that if the anolyte can be configured to supply between about 90% and about 100% of the copper to the catholyte, then the membrane essentially operates as a clean copper anode, *i.e.*, the membrane provides

copper to the catholyte without the disadvantages associated with the electrochemical reaction that takes place at the surface of the anode (sludge formation, additive consumption, planarity variations due to erosion, etc.). The anolyte of the invention generally includes a soluble copper II salt, which ~~(copper ions are~~ is not complexed with ligands like NH3, or EDTA or ~~phyrophoshoric~~ pyrophosphoric acid anions~~, as Cu transports through the membrane together with this ligand, like Cu(NH3)42+ will transport together with NH3,~~ such as copper sulfate, copper sulfonate, copper chloride, copper bromide, copper nitrate, or a blend of any combination of these salts in an amount sufficient to provide a concentration of copper ions in the catholyte of between about 0.1M and about 2.5M, or more particularly, between about 0.25 M and about 2M.

[0035] Additionally, the pH of the anolyte solution will generally be between about 1.5 and about 6, or more particularly, between about 2 and 4.8, for example. The pH is maintained in this range, as increasing the pH above this range in conventional plating configurations has been shown to cause copper hydroxide precipitation. Additionally, when the pH is below 2, and particularly if the pH is below 1.5, then the solution supports a substantial increase in the hydrogen ion (H^+) transport through the membrane from the anolyte to the catholyte. In this situation, the bulk of the plating current is carried by the H^+ ions and the copper ion transport is reduced. As such, the copper ion concentration in the catholyte decreases, potentially to a critical level that will not support plating, while simultaneously the sulfuric acid concentration in the catholyte increases. The anolyte can generally use any soluble Cu^{2+} salt, such as $CuSO_4$ (solubility 300 g/L), $CuBr_2$ (solubility more that 2 kg/L), $CuCl_2$ (solubility 700 g/L), CuF_2(47 g/L), $Cu(NO_3)_2$ (1300 g/L) etc. The selection of anions depends on their impact to prevent or minimize Cu(I) formation and anode passiviation, on penetration through the membrane etc. For instance, the anolyte can be $CuSO_4$ (0.5M) with small additions of $Cu(NO_3)$ to activate anode surface and minimize Cu(I) formation). To minimize Cu(I) formation, small additions of $Cu(ClO_3)_2$ (solubility 2 kg/L) or $Cu(IO_3)_2$ – solubility 1 g/L may be used. In similar fashion to the catholyte, the source of copper in the anolyte (aside from the anode) may be cupper sulfate pentahydrate ($CuSO_4{\circ}5H_2O$) at between about 32 g/L and 70 g/L, or at between about 0.5M and

about 0.95M. Alternatively, in a preferred embodiment, the copper source may be between about 51 g/L and about 60 g/L, preferably about 54 g/L, and at a molarity of between about 0.8M and about 0.9M, preferably about 0.85M.

[0036] The absorbent containers 404, 504 (illustrated in Figures 4 and 5) generally include an enclosed container column with at least one fluid inlet and at least one fluid outlet. The fluid path between the fluid inlet and the fluid outlet traverses an absorbent material positioned in the container or column, wherein the absorbent material is configured to contain one or more of the plating solution additives (catholyte additives, *i.e.*, levelers, suppressors, accelerators, etc.). The absorbent material is generally absorbent to the additives, and as such, the absorbent material may be saturated with the one or more additives prior to initiating the plating process. Once saturated or otherwise provided with one or more additives, the absorbent material is generally configured to desorb the additives contained therein at a known rate. More particularly, the absorbent material may be configured to desorb additives contained therein at a rate that is proportional to the fluid flow through the container or column. Alternatively, the absorbent material may leach additives in proportion to the fluid pressure applied to the container or column. Regardless of the control method for the additive desorption, when the additive concentration in the absorbent material and the additive concentration in the plating solution are equilibrated with one another, the following equation can be used:

$$CX + CY + CZ \leftrightarrow CaX + CaY + CaZ,$$

wherein CX , CY, and CZ represent the concentrations of additives X, Y, and Z in the electrolyte, CaX, CaY, and CaZ represent concentrations of additives in the absorbent material under equilibrium, and wherein $\leftrightarrow$ represents absorption and desorption of the additives (adsorption is the rightward facing arrow and desorption is the leftward facing arrow). For example, at a given temperature and given concentrations of primary chemicals into electrolyte (e.g. 50 g/L $CuSO_4$, 30 g/L H_2SO_4), there is only one combination of CaX1, CaY1, and CaZ1 for each combination of CX1, CY1, and CZ1. The rate of adsorption (Ka) and the rate of

desorption (Kd) under equilibrium are equal to one another. When one ~~will add additional amount of~~ adds absorbent (saturated with these additives at CX1, CY1, and CZ1) or additional volume of the same electrolyte into this system, all concentrations remain the same. However, when the concentration of any additive (e.g. X) in the electrolyte decreases (because of consumption, decomposition etc.), it immediately ~~rises~~ increases the desorption of X from absorbent so that the concentration of Cx in the electrolyte increases to the same value as it was before. Similarly, when the concentration of the additive increases (e.g. because of incorrect dosing, *i.e.*, from overdosing), the absorbent starts to adsorb the excess and the Cx value returns to the initial value. Thus, not only does the absorbent material operate to dispense additives into the solution, it also operates like a buffer, as it operates to compensate for changes of Cx (or other additives) into the electrolyte, thus keeping the Cx value near a desired concentration. However, in similar fashion to most buffers, the adsorbent is only capable of buffering within a proper limit. One parameter that may influence this characteristic is the ratio of the volume of the adsorbent material to the volume of the solution, *i.e.*, the higher is the adsorption capacity of absorbent regarding to X, the higher is the absorbent-to-electrolyte volume ratio and the lower is the Cx that must be maintained, the better and longer the absorbent can keep the required concentration of additive into the electrolyte bulk.

[0037] For example, during the initial plating process, both the electrolyte and absorbent material ~~contains~~ contain only additives X, Y, and Z, but during electrolysis these additives decompose on the electrodes and the concentration of breakdown products of X, Y, and Z (CBX, CBY, CBZ) into electrolyte increases. At the same time, the absorbent starts to absorb these breakdown products, decreasing their concentration into the electrolyte, which leads to substantial increase in electrolyte life-time, because the capacity of adsorbent relative to breakdown products will generally be approximately the same as X, Y, and Z.

[0038] Figure ~~5~~ 6 illustrates concentration changes of an exemplary additive X in the electrolyte or plating solution under electrolysis both when it is in contact with an absorbent saturated with additives and when there is no absorbent into the system. As

illustrated in Figure ~~5~~ 6, the presence of the absorbent material saturated with additives (generally the absorbent-electrolyte volume ratio will be between about 1:1 and about 1:10) maintains the concentration of the additives relatively constant for several days without any correction of the electrolyte, whereas without the absorbent material the concentration varies out of the processing range after several hours of electrolysis. At the same time, the accumulation of breakdown products into electrolyte becomes much slower with the absorbent material. This system (high absorbent-electrolyte volume ratio) is especially helpful when the electrolyte volume used is relatively low and there is no chemical control system that can correct additive concentration. This system provides a substantial increase in the lifetime of the electrolyte without any concentration control and correction and without any care about accumulation of breakdown into the electrolyte. After several days when the capacity of absorbent becomes exhausted, the electrolyte and adsorbent may be replaced by fresh materials.

[0040] The canister, container, column, etc. containing the absorbent material, i.e., container 405 or 505 in Figures 4 and 5, as noted above, generally includes a housing having a fluid inlet and a fluid outlet with the absorbent material positioned in the fluid path between the inlet and the outlet. The electrolyte supply may then be fed into the fluid inlet and passed through the absorbent material before exiting the container at the fluid outlet. The supply of electrolyte to the container may be through a slipstream-type configuration, for example. During the process of the fluid flowing from the inlet to the outlet, the absorbent material leaches a portion of the additives contained therein into the fluid solution flowing therethrough. Exemplary absorbent materials include activated carbon and charcoal, various polymers (e.g. polypropylene), glass, minerals, ion-exchange resins, resins for chromatography, and combinations thereof. These materials may be used in various forms within the canister, column, container, etc., (*i.e.*, they may be in the form of beads, granules, pellets, powder, fabric pads, rolls, fibers, etc). Generally, the only limitations imposed upon the absorbent material is that the material should be chemically stable in the electrolyte plating solutions, and the material should have the ability ot be cleaned

from any kind of particles or chemical components (ions, salts or organic molecules) that can contaminate the electrolyte and are detrimental to plating processes.

[0042] The method of using the absorbent materials in a plating system generally includes cleaning the absorbent material (or the absorbent blend of materials) of contaminants that otherwise might leach out in the electrolyte. Exemplary cleaning solutions include deionized water, diluted acid (e.g. H2SO4), or a complexing agent solution (e.g. EDTA) and can be used effectively. Initiating the process with equilibration of the purified absorbent with the electrolyte relative to all chemical components (salts and additives) used in the electrolyte facilitates optimal plating results, as the concentrations are easily maintained within the processing window when initiated from an equilibrium position. This process can be performed by placing the absorbent ~~is~~ into the electrolyte with required concentrations of all salts and additives. As the concentration of components in the electrolyte changes, the electrolyte may periodically be analyzed and corrected so that all concentrations become the same as the initial ~~ones~~ concentration. During the time period between analysis ~~processes~~, the absorbent material may be relied upon to maintain concentrations within the processing window. When the concentration of all additives ~~ceases to~~ does not change for a substantial period of time, ~~this is an indication that~~ the absorbent material has become saturated at given concentrations of additives. Further, when the total volume ratio of electrolyte absorbent remains the constant, the user can use the equation noted above to estimate the total amount of each additive (*i.e.*, m_X, m_Y, m_{Cl}, etc.) that must be added into electrolyte to equilibrate the electrolyte-absorbent system. The same volume of electrolyte can then be supplemented with the same amount of absorbent, m_X of additive X, m_Y of Y, etc., ~~in order~~ to maintain the desired concentrations in the mixture for a time required to reach the adsorption equilibrium.

[0043] In another embodiment of the invention the absorbent material may be treated (saturated with additives) and then positioned ~~placed into~~ in the electrolyte tank or in a column disposed ~~into~~ in the electrolyte loop of the electrochemical cell. The electrolyte-to-absorbent volume ratio in the electrodeposition tool can be from

between about 1:1 to about 20:1. To use this system without a chemical control system, this ratio will generally be relatively high, from between about 1:1 to about 1:5. To improve the stability of the bath and increase the lifetime of the electrolyte, lower volume ratios may be used.